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(54) **PROCEDE PERMETTANT DE RETRAITER DES MATERIAUX
CONTENANT DES METAUX PRECIEUX PAR SEPARATION
ET FRACTIONNEMENT CHROMATOGRAPHIQUES**(54) **METHOD FOR REPROCESSING MATERIALS CONTAINING
PRECIOUS METALS BY MEANS OF CHROMATOGRAPHIC
SEPARATION AND FRACTIONATION**

(57) L'invention concerne un procédé permettant de retraiter des matériaux contenant des métaux précieux, notamment des concentrés primaires de métallurgie. Ce procédé consiste à soumettre ces matériaux, à température élevée et chronologiquement, à un traitement oxydant, à un traitement réducteur et à une chloration réalisée à l'aide d'agents gazeux. L'or et les métaux du groupe platine restent sous forme de résidu. Ce résidu est soumis à une lixiviation acide oxydante. La fraction d'or est d'abord séparée de la phase liquide par voie chromatographique, ensuite le liquide restant est fractionné par voie chromatographique pour obtenir les différents métaux du groupe platine. Le fractionnement est réalisé par mouvement relatif d'un lit de particules se présentant sous forme d'enveloppe d'un cylindre par rapport à au moins un point d'alimentation en liquide.

(57) The invention relates to a method for reprocessing materials containing precious metals especially from metallurgic primary concentrates in which the materials are subjected to an increased temperature in the sequence of an oxidized treatment, a reducing treatment and a chlorination by the application of gaseous treatment media. Gold and the platinum group metals remain as residual matter with the characteristic that the residual matter is subjected to oxidized acid leaching. The gold portion is chromatographically separated first from the liquid phase and the remaining liquid is then chromatographically fractionated into the individual platinum group metals, whereby the fractionation is carried out by means of relative movement between a particle bed in the form of a cylinder jacket and at least one output position for the liquid.



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<p>(51) Internationale Patentklassifikation ⁶ : C22B 11/00, 3/42, 11/06, B01D 15/08, B01J 39/06</p>	A1	<p>(11) Internationale Veröffentlichungsnummer: WO 99/13115</p> <p>(43) Internationales Veröffentlichungsdatum: 18. März 1999 (18.03.99)</p>
<p>(21) Internationales Aktenzeichen: PCT/AT98/00206</p> <p>(22) Internationales Anmeldedatum: 28. August 1998 (28.08.98)</p> <p>(30) Prioritätsdaten: A 1534/97 11. September 1997 (11.09.97) AT</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): PRIOR ENGINEERING AG [CH/CH]; Zollikerstrasse 141, CH-8008 Zürich (CH).</p> <p>(72) Erfinder; und</p> <p>(75) Erfinder/Anmelder (nur für US): PRIOR, Adalbert [AT/AT]; Neuburgstrasse 8, A-6841 Götzis (AT).</p> <p>(74) Anwälte: COLLIN, Hans usw.; Mariahilferstrasse 50, A-1070 Wien (AT).</p>	<p>(81) Bestimmungsstaaten: AU, CA, KR, RU, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p>	
<p>(54) Title: METHOD FOR REPROCESSING MATERIALS CONTAINING PRECIOUS METALS BY MEANS OF CHROMATOGRAPHIC SEPARATION AND FRACTIONATION</p> <p>(54) Bezeichnung: VERFAHREN ZUM AUFARBEITEN VON EDELMETALLHALTIGEN MATERIALIEN MIT CHROMATOGRAPHISCHER ABTRENNUNG UND FRAKTIONIERUNG</p> <p>(57) Abstract</p> <p>The invention relates to a method for reprocessing materials containing precious metals especially from metallurgic primary concentrates in which the materials are subjected to an increased temperature in the sequence of an oxidized treatment, a reducing treatment and a chlorination by the application of gaseous treatment media. Gold and the platinum group metals remain as residual matter with the characteristic that the residual matter is subjected to oxidized acid leaching. The gold portion is chromatographically separated first from the liquid phase and the remaining liquid is then chromatographically fractionated into the individual platinum group metals, whereby the fractionation is carried out by means of relative movement between a particle bed in the form of a cylinder jacket and at least one output position for the liquid.</p> <p>(57) Zusammenfassung</p> <p>Vorgeschlagen wird ein Verfahren zum Aufarbeiten von edelmetallhaltigen Materialien, insbesondere von metallurgischen Primärkonzentraten, bei dem die Materialien bei erhöhter Temperatur in der Reihenfolge einer oxidierenden Behandlung, einer reduzierenden Behandlung und einer Chlorierung unter Einsatz von gasförmigen Behandlungsmedien unterzogen werden, wobei Gold und die Platingruppenmetalle im Rückstand verbleiben, mit dem Kernzeichen, daß der Rückstand einer oxidierenden Säurelaugung unterzogen, aus der flüssigen Phase zuerst der Goldanteil chromatographisch abgetrennt und die verbleibende Flüssigkeit dann chromatographisch in die einzelnen Platingruppenmetalle fraktioniert wird, wobei die Fraktionierung unter Relativbewegung zwischen einem Teilchenbett in Form eines Zylindermantels und mindestens einer Aufgabestelle für die Flüssigkeit durchgeführt wird.</p>		

Patent Claims:

1. A method for dressing materials containing precious metals, in particular metallurgical primary concentrates, wherein the materials are subjected to an oxidising treatment, a reducing treatment and chlorination using gaseous treatment media in this order at elevated temperatures, gold and the platinum group metals remaining in the residue, characterised in that the residue is subjected to oxidative leaching with acid, in that the gold is first separated from the liquid phase by chromatography, and in that the remaining liquid is then fractionated into the individual platinum group metals by chromatography, while carrying out fractionation under relative movement between a particle bed taking the form of a cylinder jacket and at least one application site for the liquid.
2. The method according to claim 1, characterised in that the gold is separated on a vinylstyrene resin.
3. The method according to claim 1 or claim 2, characterised in that fractionation is carried out at a gel of a dextran-type polysaccharide, at a cross-linked polymethacrylate gel, or at a cross-linked polyacrylamide gel.
4. The method according to any of claims 1 to 3, characterised in that the oxidative leaching with acid is carried out with hydrochloric acid containing chlorine gas.
5. The method according to any of claims 1 to 4, characterised in that the remaining liquid is oxidised to a redox potential higher than about 700 mV, in particular 800 to 1200 mV, before fractionation.
6. The method according to claim 5, characterised in that oxidation is carried out in an electrochemical fashion.

The present invention relates to a process for dressing materials containing precious metals, in particular metallurgical primary concentrates, wherein the materials are subjected to an oxidising treatment, a reducing treatment and chlorination using gaseous treatment media in this order at elevated temperatures, gold and the platinum group metals remaining in the residue.

This method is known to specialists as the chloroxomate process and is described in WO 96/17097. Its aim is to eliminate the accompanying metals and other contents from raw materials containing gold and platinum group metals in the gaseous phase, so that what finally remains is a residue enriched in gold and platinum group metals. The raw materials usually are concentrates resulting from the smelting of Ni, Cu or Zn, and contain for instance S, Se, Ag, Te, Cu, Ni, As, Sb, and Pb as accompanying metals and impurities, respectively. First the material is treated with oxidising gas (oxygen or oxygen-containing gas mixtures, as for instance 20% O₂ in inert gas or in air) at 200 to 800, preferably 400 to 500°C, in the course of which S and Se are primarily eliminated, but metal oxides are formed and volatile oxygen compounds are eliminated as well.

Scavenging with an inert gas, for instance N₂ and/or CO₂, is followed by treatment with reducing gas (hydrogen or hydrogen-containing gas, for instance nitrogen with at least 1% H₂) at 200 to 1000, preferably 600 to 800°C, primarily in order to reduce previously formed metal oxides to metal again. Subsequently it is again possible to scavenge with an inert gas, and finally chlorination is carried out with chlorine gas at 800 to 1300, preferably 900 to 1150 °C, in the course of which volatile chlorides (e.g. of Cu, Ni, Ag) escape. After cooling down of the material washing is carried out in order to eliminate non-volatile chlorides, and a residue is obtained which is a concentrate of gold and platinum group metals also including SiO₂, for instance.

According to the invention the residue is submitted to oxidative leaching with acid, the gold is first separated from the liquid phase by chromatography, and the remaining liquid is subsequently fractionated into the individual platinum group metals by

chromatography, fractionation being carried out under relative movement between a particle bed in the form of a cylinder jacket and at least one place for applying the liquid.

Oxidative leaching with acid is advantageously carried out with hydrochloric acid containing chlorine gas, or for instance with hydrochloric acid and H_2O_2 or, as usual, with aqua regia, gold and the platinum group metals being dissolved.

From this solution the gold is first separated off by chromatography in known fashion. Vinylstyrene resins, in particular Amberlite XAD7, are known as ion exchange resins selective for gold.

Following the removal of gold, the remaining liquid is fractionated into the individual platinum group metals by means of chromatography, fractionation being carried out under relative movement between a particle bed taking the form of a cylinder jacket and at least one site for the application of the liquid.

The chromatographic technique wherein relative movement is provided between a particle bed taking the form of an upright cylinder jacket and at least one site for the application of liquid feeding material, arranged at the head thereof, the individual components passing the particle material in spirally wound paths and leaving in various circumferential regions along the lower periphery of the cylinder jacket, is a continuous process and is called annular chromatography. The international abbreviation for continuous annular chromatography is CAC.

Known apparatus for CAC include devices wherein the particle bed is immobile as well as those wherein the particle bed rotates with respect to site(s) of application and collection sites. An example for reference describing devices of the second type in detail as well as giving a review of the different methods of chromatography is EP-A- 371 648 of Union Oil of California.

Surprisingly, it has been found that this technique in combination with the chloroxamate process not only results in excellent product yields, but also in excellent separation.

Particularly well suited for fractionating the platinum group metals are organic ion exchangers in the form of macroporous spheric gels, in particular those on the basis of 1) dextran-type polysaccharides, 2) cross-linked polymethacrylates, and 3) cross-linked polyacrylamides.

Examples for products of item 1) are the Sephadex G ion exchangers of Pharmacia (Sweden), which are dextrans cross-linked with epichlorohydrin. Examples for products of item 2) are Toypearl HW ion exchangers of Tosohaas (Japan, USA), which are polymethylacrylates cross-linked with ethylene glycol. Examples for products of item 3) are Biogel P ion exchangers of Biorad (USA) which are copolymerisates of acrylamide and N,N'-methylene-bis-acrylamide.

The first stage of the process according to the invention, i.e. the treatment of the basic material in gaseous phase, results in a weight loss of 30 to 35 % - about 95 % of the accompanying metals are eliminated in the course of it. A loss of gold of about 2 % and a loss of palladium of about 0,5 to 1 % is inevitable here as well.

Practically no losses are incurred at the subsequent chromatographic removal of gold and chromatographic fractionation of platinum group metals - the precious metal content of the column effluents is below 50 ppm, the effluents being recycled, of course.

For CAC fractionation of the platinum group metals it is advantageous to bring the feed to an oxidation potential of at least 700 mV, in particular 800 to 1200 mV, in order to

guarantee that I_r^{III} is converted to I_r^{IV} . This oxidation can be done chemically, as usual, or electrochemically in the feeder head of the CAC column (anodic oxidation).

Example

Basic material: precious metal concentrate "Impala Fe-Grain"

1) Chloroxomate stage: Finely ground concentrate was pelleted with 1,56 % by weight of corn starch. The pellets were thermally treated under gas scavenging as follows:

Table 1

time (minutes)	gas	flow rate (l/h)	temperature (°C)
-15 (heating)	N ₂	15	450
-15	N ₂	15	450
-15	N ₂ /H ₂	15 (each)	550
-15	N ₂	15	550
-30	O ₂	25	550
-15	N ₂	15	850
-45	N ₂ /H ₂	15 (each)	850
-10 (heating)	N ₂	15	1050
-160	Cl ₂ /N ₂	footnote	1050
-15	N ₂	15	800
-15	N ₂ /H ₂	15 (each)	800
-90	N ₂	10	room temperature

Footnote: for 30 min N₂:Cl₂ = 15:25 l/h, then for 130 min Cl₂ for 5 min each at 16l/h, in between each time N₂ for 1 min at 50 l/h.

The following were observed: when heating to 450°C white vapours, and at 450°C dehydration; during the oxidation treatment white vapours; during treatment with H₂/N₂

at 850 °C first white, then red, then dark-brown vapours as well as dehydration; and during Cl_2 treatment light brownish-grey vapour. The weight loss was 45,9 % by weight.

2) Oxidative leaching of the residue with acid: The residue was boiled in HCl conc. under reflux for 3 hours while passing Cl_2 therethrough. After 3 hours the potential of the solution was measured to be 1053 mV. The solution was separated from the undissolved matter by filtration, diluted with water 1:1, and the gold content was removed by passing the solution over an Amberlite XAD7 column. The remaining solution was again oxidised by boiling under reflux for 2 hours while bubbling Cl_2 therethrough and, at 1 ml/min, applied as feed onto a CAC column which had been packed with Toyopearl HW 40 F, and eluted with 1 mol/l HCl (15 ml/min).

Type: bed rotates with respect to feed and fraction collector

bed thickness: 0,65 cm

bed height: 38,0 cm

bed cross-section: 24,4 cm²

rotation: 95°/h

Two eluate fractions were removed at the bottom of the column - the first at an angle of approximately 70°, and the second at an angle of approximately 140° with respect to the feeding site, which fractions have the following composition as compared to the feed, given in mg/l:

Table 2

	basic material (mg/l)	1st fraction (mg/l)	2nd fraction (mg/l)
Ag	257	< 1	24
Ru	5074	267	104
Au	< 1	< 1	< 1
Pd	14991	< 1	4230
Pt	11516	< 1	< 1
Ir	3382	172	89
Rh	9485	5159	< 1
Fe	29	1	< 1
Cu	59	17	< 1
Ni	46	28	< 1
Co	2	< 1	< 1
Pb	3	< 1	< 1
Zn	1	2	< 1
Si	23	2	6
Se	51	5	8
Te	17	3	< 1
As	20	< 1	< 1
P	24	8	3
Re	4	< 1	< 1

It can be seen that rhodium moves into the first fraction and palladium moves into the second fraction, these two metals thus being separable from each other in this mode. Pt remains in the column.